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Unexpected course of the attempted conversions of ferrocenyl(hetaryl)methanols into thiols using Lawesson′s reagent

Grzegorz Mlostoń[1], Róża Hamera-Fałdyga[1], and Heinz Heimgartner[2]

[a] Department of Organic and Applied Chemistry, University of Łódź, Tamka 12, PL-91-403 Łódź, Poland; [b] Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

Dedicated to Prof. Harry R. Hudson in memoriam

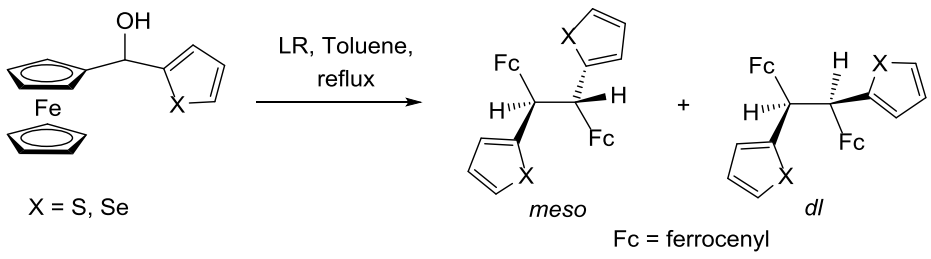
ABSTRACT

A series of secondary methanols bearing ferrocenyl and a hetaryl substituent was tested in reactions with Lawesson's reagent (LR) aimed at the preparation of respective methane thiols. The study showed that in boiling toluene after only few minutes the starting alcohols were consumed and unexpectedly, depending on the type of hetaryl substituent, tetra-substituted ethane or disubstituted methane derivatives were obtained in good to excellent yields. The presence of the ferrocene moiety is crucial for the observed reaction courses.

KEYWORDS

Lawesson's reagent, secondary alcohols, thiols, ferrocene derivatives, thiophene derivatives, selenophene derivatives, C,C-coupling

Graphical Abstract

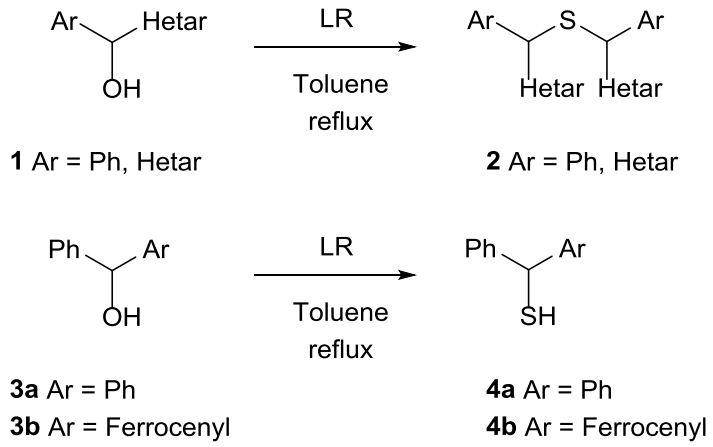


CONTACT Grzegorz Mlostoń e-mail: gmloston@uni.lodz.pl mail: Department of Organic and Applied Chemistry, University of Łódź, Tamka 12, PL-91-403 Łódź, Poland

Introduction

Ferrocene and its derivatives are widely applied as substrates and building blocks for the synthesis of ferrocenyl-containing more complex organic molecules with importance in materials chemistry, medicinal chemistry, catalysis, etc.[1] In a very recent review summarizing its chemistry, ferrocene has been named as an 'exceptional molecule'.[1f] Unlike disubstituted ferrocenyl methanols, their sulfur analogues, i.e., corresponding ferrocenyl methanethiols, are little known. Although the reduction of thioketones is not a general method for the preparation of secondary thiols, we showed that diferrocenyl thioketone reacts with LDA in THF to give the corresponding diferrocenylmethanethiolate, which upon treatment with methyliodide gave diferrocenylmethyl methyl sulfide.[2]

In recent papers we described efficient methods for the preparation of aryl, hetaryl and ferrocenyl ketones,[3] which were transformed into the corresponding disubstituted methanols.[4] Selected aryl hetaryl and dihetaryl methanols **1** were used for the reaction with Lawesson's reagent (LR) in order to prepare the respective thiols.[4] Unexpectedly, instead of the latter, sulfides of type **2** were obtained as exclusive products in all cases (Scheme 1). This unexpected observation was explained by the presence of a hetaryl ring (i.e., furan-2-yl, thiophen-2-yl, or selenophen-2-yl) in the starting alcohol **1**. These results differ from that obtained with benzhydryl alcohol (**3a**), which in wet toluene was smoothly converted into benzhydryl thiol **4a**.[5] Interestingly, the analogous reaction with ferrocenyl(phenyl)methanol (**3b**) in dry toluene led to ferrocenyl(phenyl)methanethiol (**4b**).[4]

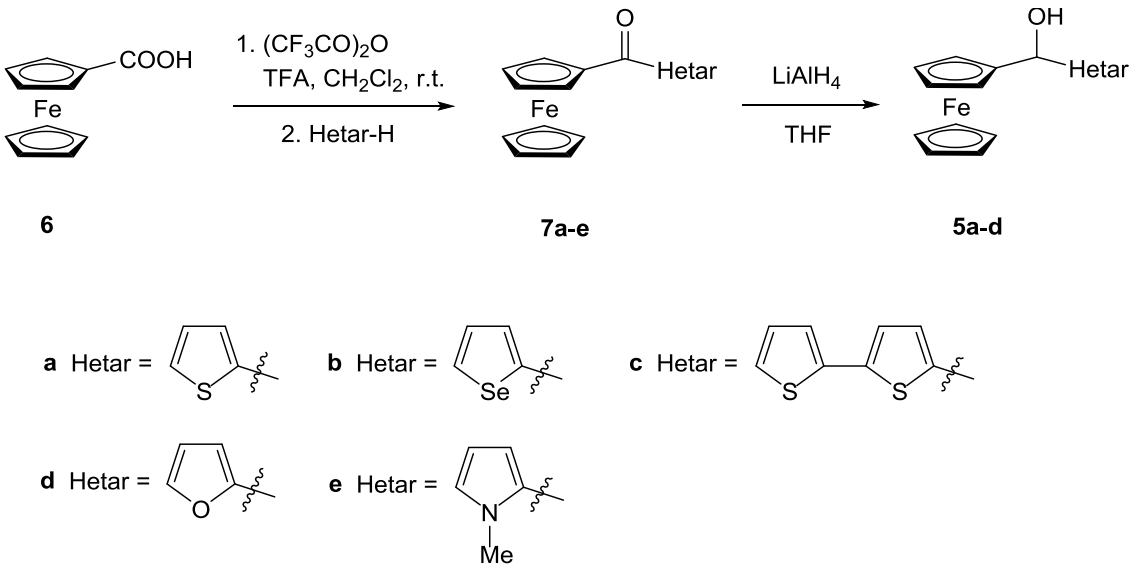


Scheme 1. Reactions of aryl hetaryl, diphenyl, and ferrocenyl(phenyl)methanols with Lawesson's reagent (LR).

These observations prompted us to study the reaction of ferrocenyl(hetaryl)methanols **5** with Lawesson's reagent (LR) under water-free conditions.

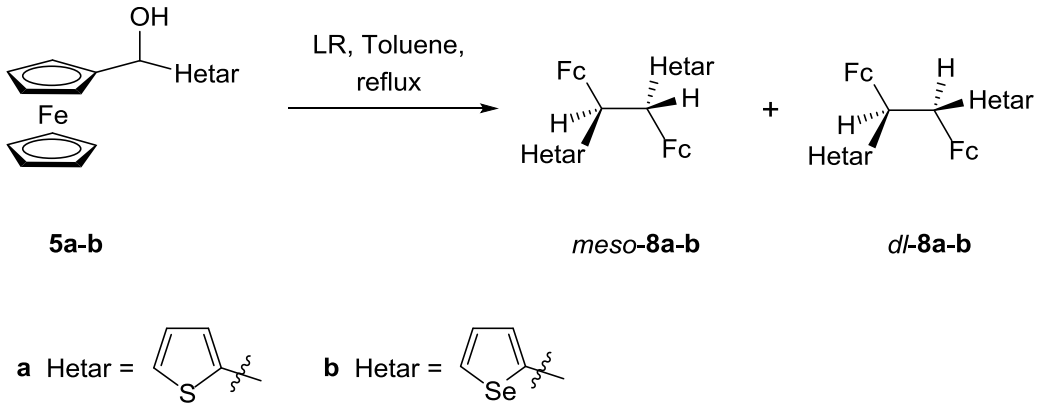
Results and discussion

The preparation of non-symmetrical ferrocenyl hetaryl ketones **7** was achieved via Friedel-Crafts acylation of furan, *N*-methylpyrrole, thiophene, selenophene, and 5-(thiophen-2-yl)thiophene, respectively, with the in situ-generated mixed anhydride of ferrocenoic acid (**6**) and trifluoroacetic acid (TFA) in dichloromethane at room temperature[3b] (Scheme 2). Reduction of ketones **7a-d** by treatment with $LiAlH_4$ in THF afforded the desired ferrocenyl hetaryl methanols **5a-d** in good yields. All attempts to reduce the ferrocenyl (N-methyl)pyrrol-1-yl ketone (**7e**) were unsuccessful and in all experiments only a mixture of unidentifiable decomposition products was obtained.



Scheme 2. Synthesis of ferrocenyl(hetaryl)methanols **5a**-**d**.

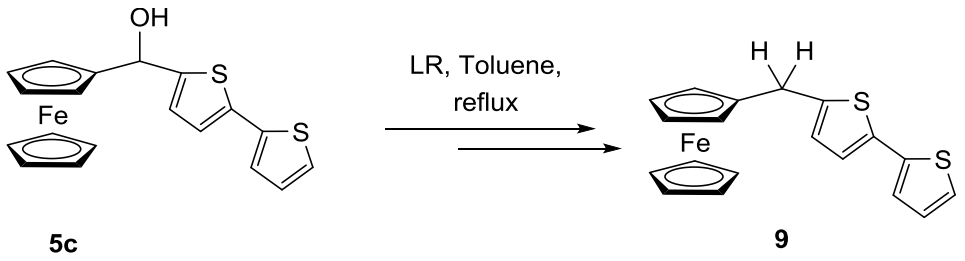
The reaction of ferrocenyl(thiophen-2-yl)methanol (**5a**) and LR in boiling dry toluene aimed at the preparation of the corresponding methanethiol was complete after 20 min. The chromatographic separation gave a single product isolated as a yellow solid. The ^{1}H NMR spectrum revealed the presence of two isomeric products in ca. 1:1 ratio. The most characteristic signals are two singlets at 4.25 and 4.22 ppm. In addition, the two isomeric products showed two sets of the typical signals of ferrocenyl and thiophen-2-yl residues. The ^{13}C NMR spectrum confirmed the presence of two isomeric compounds in comparable amounts. In that case, two signals appeared at 146.3 and 145.2 ppm as well as at 90.6 and 89.8 ppm, which are attributed to C(2)-atoms of the thiophene rings and C(1) of the ferrocenyl unit, respectively. Based on these data, the isolated product was not the expected methanethiol. However, the structure of a dibenzhydryl-type sulfide[4] has to be excluded as the elemental analysis as well as the HR-MS proved the molecular formula $C_{30}H_{26}Fe_2S_2$, which corresponds with the structure of a product formed from two molecules of the expected thiol after elimination of S_2. It seems likely that the isolated compounds form a mixture of the *meso* and *dl* diastereoisomers of 1,2-diferrocenyl-1,2-di(thiophen-2-yl)ethane (**8a**) (Scheme 3).



Scheme 3. Reaction of ferrocenyl(hetaryl)methanols **5a-b** with Lawesson's reagent (LR).

A similar reaction course leading to a mixture of diastereoisomeric products was also observed with ferrocenyl(selenophen-2-yl)methanol (**5b**). In both cases, the attempted separation of the diastereoisomers by column chromatography or fractional crystallization was unsuccessful.

Unexpectedly, treatment of ferrocenyl(2,2'-bithiophen-5-yl)methanol (**5c**) with LR under identical conditions led to the ferrocenylmethane derivative **9**, which was isolated chromatographically in 49% yield. Its structure was confirmed by means of spectroscopic methods and elemental analysis. In the ^{1}H NMR spectrum, the diagnostic signal attributed to the CH_2 group absorbed at 3.87 ppm.

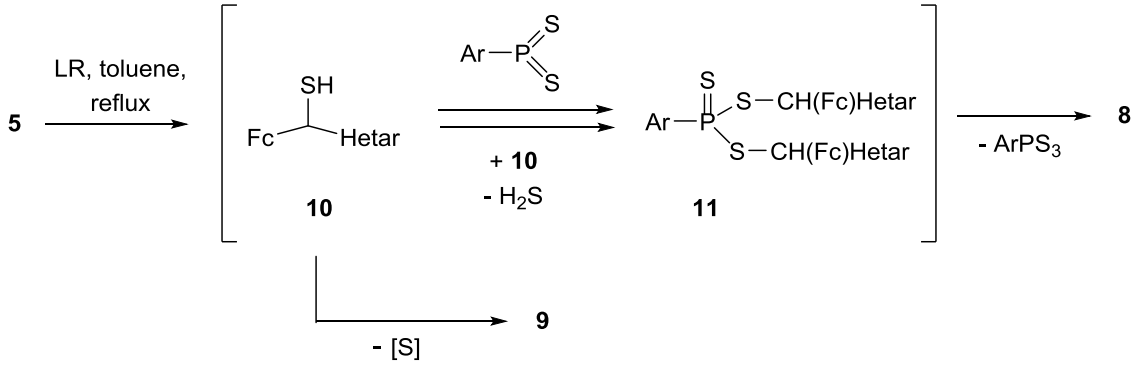


5c **9**

Scheme 4. Unexpected formation of ferrocenylmethane derivative **9** from the secondary alcohol **5c**.

In extension of the study, reactions of LR with ferrocenyl(furan-2-yl)methanol (**5d**) were also carried out, but in this case, a complex mixture of unidentifiable products was obtained.

The unexpected results deserve a mechanistic explanation, which comprises a multistep conversion. It is likely that the first step is the formation of the expected methanethiols **10**, which are trapped by the monomeric unit of LR yielding the corresponding trithiophosphonates **11**, similar to the compound isolated in the reaction with benzhydryl alcohol[4] (Scheme 4). Apparently, the behavior of these derivatives depends on the type of substituent present in the [Ar_2CH] fragment. In contrast to aryl/hetaryl representatives, the ferrocenyl/hetaryl analogues easily undergo thermal decomposition by the cleavage of the C–S bonds leading to the isolated products of type **8**.



Scheme 5. Proposed reaction sequence of the formation of products **8** and **9**.

The final step of the conversion is believed to occur via radical intermediates, and the presence of ferrocenyl and hetaryl moieties is of crucial importance for their appearance. The role of ferrocenyl residues for a similar transformation, which also may occur via a radical pathway, was evidenced in a recent report.[6]

However, in the case of **5c**, formal desulfurization of the initially formed thiol **10c** leads to the isolated methane derivative **9**. At the moment, it seems difficult to formulate a convincing mechanism of this intriguing transformation. However, steric hindrance in the intermediate radical and more difficult formation of the new C-C bond can be an important factor for the formation of **9** instead of the 'dimeric' **8**.

Conclusions

The presented study showed that the type of substituents in secondary methanols of the benzhydryl type strongly determines the course of the reaction with LR and, therefore, the type of the final product. Benzhydryl alcohol and ferrocenyl(phenyl)methanol react to give the corresponding thiols.[4] On the other hand, hetaryl(phenyl) and dihetarylmethanols are converted into symmetrical sulfides.[4] Finally, starting with ferrocenyl(hetaryl)methanols, tetrasubstituted ethanes are obtained in the cases of hetaryl = thiophen-2-yl or selenophen-2-yl. In addition, treatment of ferrocenyl(2,2'-bithiophen-5-yl)methanol with LR led, unexpectedly, to the ferrocenylmethane derivative **9**. These different reaction courses can be rationalized by the assumption that the presence of the ferrocenyl moiety and a hetaryl substituent strongly influence the reactivity of the reactive intermediates appearing in these transformations. In the case of the present study, both the ferrocenyl and hetaryl residues are required to support the formation of the new C–C bond of products **8**. It seems likely that in reactions carried

out with **5a** and **5b** the latter reaction proceeds via the intermediate trithiophosphonate **11** and a radical mechanism governs the reaction. On the other hand, the formation of methane derivative **9** is supposed to take place via the formal desulfurization of the initially formed methanethiol **10c**. All these results point out that the presence of the ferrocenyl moiety is required to enable formation of products of type **8** or **9**. The presented study confirms once more that ferrocene and its derivatives are truly 'exceptional molecules', which may undergo diverse unexpected transformations.[1f]

Experimental

General procedure

All solvents were dried over appropriate drying agents and distilled before use. The ^{1}H and ^{13}C NMR were measured on a Bruker Avance III instrument (600 and 150 MHz, respectively), using the solvent ($CDCl_3$) signal as reference. The IR spectra (KBr pellets) were recorded on a Nexus FT-IR spectrophotometer. The elemental analyses were recorded on a Vario Micro Cube. HRMS (ESI) were recorded on a Bruker maXis spectrometer. Flash column chromatography (FCC) was carried out using Silica gel 60 (Sigma-Aldrich, 230–400 mesh). Melting points were determined in a capillary using a Stewart® SMP30 and they are uncorrected. The notation Fc in this study represents ferrocenyl. Applied ferrocenyl substituted ketones were obtained by known methods according to the literature protocols.[3b] Other reagents used were commercially available.

Synthesis of ferrocenyl(hetaryl)methanols 5

To the solution of a ketone **7** (1 mmol) in THF (5 mL), $LiAlH_4$ (2M, 0.6 mL) was added portion-wise. The progress of the reaction was monitored by thin layer chromatography (TLC). The mixture was stirred until the ketone was consumed. After completion of the reaction, a saturated solution of $MgSO_4$ (4 mL) was added. The precipitate was filtered and the filtrate was concentrated. The crude product was purified by FCC (silica gel, CH_2Cl_2:hexane 3:7).

Ferrocenyl(thien-2-yl)methanol (5a)

Yield: 267 mg (90%). Yellow solid. M.p.: 69.4–71.2 °C. ^{1}H NMR: δ 2.56 (d, $J_{H,H}$ = 4.2 Hz, OH), 4.21–4.22 (m, 1CH(Fc)), 4.23–4.24 (m, 1 CH(Fc)), 4.26 (s, 5CH(Fc)), 4.28–4.30 (m, 2CH(Fc)), 5.74 (d, $J_{H,H}$ = 3.6 Hz, CH), 6.94–6.97 (m, $2CH_{arom.}$), 7.25 (dd, $^{4}J_{H,H}$ = 1.8 Hz, $^{3}J_{H,H}$ = 4.8 Hz, $CH_{arom.}$) ppm. ^{13}C NMR: δ 66.3, 67.2, 68.1, 68.2, 68.3 (5C,

CH(Fc), CH-OH), 68.6 (s, 5C, CH(Fc)), 93.4 (1C, C(Fc)), 124.4, 124.6, 126.3 (3C, $CH_{arom.}$), 147.3 (1C, $C_{arom.}$) ppm. IR: υ 3373 (m, OH), 3101 (m), 3069 (m), 2923 (w), 2854 (w), 1456 (m), 1441 (m), 1407 (m), 1292 (m), 1228 (m), 1189 (m), 1106 (m), 1045 (m), 998 (s), 980 (s), 922 (m), 823 (m), 811 (m), 761 (m), 712 (vs), 511 (s), 494 (s) cm^{-1}. Anal. calcd. for $C_{15}H_{14}FeOS$ (298.18): C 60.42, H 4.73, S 10.75, found: C 60.52, H 4.93, S 10.74.

Ferrocenyl(selenophen-2-yl)methanol (5b)

Yield: 241 mg (70%). Yellow solid. M.p.: 43.6–45.6 °C. ^{1}H NMR: δ 2.72 (d, $J_{H,H}$ = 3.6 Hz, OH), 4.22–4.23 (m, 1CH(Fc)), 4.24–4.25 (m, 1CH(Fc)), 4.28 (s, 5CH(Fc)), 4.30–4.31 (m, 1CH(Fc)), 4.32–4.33 (m, 1CH(Fc)), 5.74 (d, $J_{H,H}$ = 3.6 Hz, CH), 7.12 (d, $^3J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 7.20 (dd, $^3J_{H,H}$ = 3.6 Hz, $^3J_{H,H}$ = 5.4 Hz, $CH_{arom.}$), 7.94 (dd, $^4J_{H,H}$ = 0.6 Hz, $^3J_{H,H}$ = 5.4 Hz, $CH_{arom.}$) ppm. ^{13}C NMR: δ 65.9, 67.2, 68.0, 68.1, 69.9 (5C, CH(Fc), CH-OH), 68.5 (s, 5C, CH(Fc)), 93.7 (1C, C(Fc)), 126.0, 128.7, 129.7 (3C, $CH_{arom.}$), 154.9 (1C, $C_{arom.}$) ppm. IR: υ 3402 (m, OH), 3091 (m), 3056 (w), 2923 (w), 2892 (w), 2851 (w), 2369 (w), 2255 (w), 2059 (w), 1638 (w), 1537 (w), 1458 (m), 1407 (m), 1388 (m), 1347 (m), 1292 (m), 1223 (m), 1185 (m), 1138 (m), 1103 (m), 1043 (s), 998 (s), 975 (m), 919 (m), 824 (s), 808 (s), 777 (m), 704 (s), 504 (s) cm^{-1}. Anal. calcd. for $C_{15}H_{14}FeOSe$ (345.08): C 52.21, H 4.09, found: C 52.15, H 4.16.

Ferrocenyl(2,2'-bithiophen-5-yl)methanol (5c)

Yield: 373 mg (98%). Yellow solid. M.p.: 72.0–74.0 °C. ^{1}H NMR: δ 2.53 (d, $J_{H,H}$ = 3.6 Hz, OH), 4.23–4.26 (m, 2 CH(Fc)), 4.28 (s, 5CH(Fc)), 4.31 (brs, 1 CH(Fc)), 4.33 (brs, 1 CH(Fc)), 5.67 (d, $J_{H,H}$ = 3.6 Hz, CH), 6.83–6.86 (m, 1 $CH_{arom.}$), 6.98–7.02 (m, 2 $CH_{arom.}$), 7.13–7.16 (m, 1 $CH_{arom.}$), 7.18–7.21 (m, 1 $CH_{arom.}$) ppm. ^{13}C NMR: δ 66.2, 67.3, 68.2, 68.4 (4C, CH(Fc)), 68.3 (1C, CH-OH), 68.7 (s, 5C, CH(Fc)), 93.2 (1C, C(Fc)), 123.0, 123.5, 124.2, 125.0, 127.7 (5C, $CH_{arom.}$), 136.7, 137.5, 146.3 (3C, $C_{arom.}$) ppm. IR: υ 3411 (m, OH), 3098 (m), 3066 (m), 1426 (m), 1375 (m), 1106 (m), 1036 (s), 998 (m), 840 (m), 796 (vs), 694 (vs), 501 (m), 479 (s) cm^{-1}. Anal. calcd. for $C_{19}H_{16}FeOS_2$ (380.30): C 60.01, H 4.24, S 16.86, found: C 60.12, H 4.35, S 16.71.

Ferrocenyl(furan-2-yl)methanol (5d)

Yield: 256 mg (91%). Yellow solid. M.p.: 60.8–62.4 °C. ^{1}H NMR: δ 2.38 (d, $J_{H,H}$ = 4.8 Hz, OH), 4.14–4.23 (m, 7 CH(Fc)), 4.26–4.32 (m, 2 CH(Fc)), 5.50 (d, $J_{H,H}$ = 4.8 Hz,

CH), 6.24–6.26 (m, 1 $CH_{arom.}$), 6.35 (dd, $^3J_{H,H}$ = 3.0 Hz, $^4J_{H,H}$ = 1.8 Hz, $CH_{arom.}$), 7.41 (brs, 1 $CH_{arom.}$) ppm. ^{13}C NMR: δ 66.2, 67.0, 67.3, 68.1, 68.2 (5C, CH(Fc), CH-OH), 68.6 (s, 5C, CH(Fc)), 90.4 (1C, C(Fc)), 106.4, 110.1, 141.8 (3C, $CH_{arom.}$), 155.7 (1C, $C_{arom.}$) ppm. IR: υ 3370 (s, OH), 3142 (m), 3120 (m), 3094 (m), 3078 (m), 2916 (w), 1617 (w), 1505 (m), 1459 (m), 1432 (m), 1382 (m), 1299 (s), 1225 (s), 1146 (s), 1105 (s), 1076 (m), 1045 (s), 1023 (s), 1001 (vs), 948 (m), 885 (s), 827 (s), 812 (vs), 788 (vs), 749 (vs), 601 (s), 519 (vs), 499 (vs), 482 (vs) cm^{-1}. Anal. calcd. for $C_{15}H_{14}FeO_2$ (282.12): C 63.86, H 5.00, found: C 63.73, H 4.98.

Synthesis of ferrocenyl substituted ethanes 8 and methane 9

To the solution of an alcohol **5** (1 mmol) in toluene (5 mL), Lawesson's reagent (0.6 mmol, 0.24 g) was added. The mixture was stirred at reflux for 20 min. Then, the solvent was evaporated and the crude product was purified by FCC (silica gel, CH_2Cl_2:hexane 3:7).

1,2-Diferrocenyl-1,2-di(thiophen-2-yl)ethane (8a)

Yield: 261 mg (93%). Yellow solid. M.p.: decomposition (>176 °C). ^1H NMR (two diastereoisomers, ca. 1:1): δ 3.70–3.71 (m, 1CH(Fc)), 3.78–3.79 (m, 1CH(Fc)), 3.82 (s, 5CH(Fc)), 3.86 (s, 5CH(Fc)), 3.93–3.94 (m, 1CH(Fc)), 3.95–3.96 (m, 1CH(Fc)), 4.03–4.04 (m, 1CH(Fc)), 4.05–4.06 (m, 1CH(Fc)), 4.07–4.08 (m, 1CH(Fc)), 4.12–4.13 (m, 1CH(Fc)), 4.22 (s, CH), 4.25 (s, CH), 6.65–6.68 (m, 2$CH_{arom.}$), 6.84 (dd, $^4J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 6.90 (dd, $^4J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 7.09 (dd, $^4J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 5.4 Hz, $CH_{arom.}$), 7.14 (dd, $^4J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 5.4 Hz, $CH_{arom.}$) ppm. ^{13}C NMR (two diastereoisomers, ca. 1:1): δ 51.5, 51.6 (2C, CH), 66.6, 66.9, 67.3, 67.6, 67.8, 68.7, 69.5, 70.4 (8C, CH(Fc)), 68.5 (s, 5C, CH(Fc)), 68.6 (s, 5C, CH(Fc)), 89.8, 90.6 (2C, C(Fc)), 122.6, 122.8, 125.5, 125.6, 125.7, 125.8 (6C, $CH_{arom.}$), 145.2, 146.3 (2C, $C_{arom.}$) ppm. IR: υ 3088 (m), 2892 (m), 1768 (w), 1632 (w), 1597 (w), 1534 (w), 1439 (m), 1413 (m), 1277 (w), 1233 (m), 1109 (s), 1046 (s), 1027 (s), 1002 (s), 926 (m), 853 (m), 808 (vs), 698 (vs), 482 (vs) cm^{-1}. Anal. calcd. for $C_{30}H_{26}Fe_2S_2$ (562.35): C 64.07, H 4.66, S 11.40 found: C 64.05, H 4.79, S 11.39. HRMS (ESI): *m/z* calcd. for $C_{30}H_{26}Fe_2S_2$ 562.01693; found 562.01748.

1,2-Diferrocenyl-1,2-di(selenophen-2-yl)ethane (8b)

Yield: 200 mg (61%). Yellow solid. M.p.: decomposition (>180 °C). ^1H NMR (two diastereoisomers, ca. 1:1): δ 3.88 (s, 5CH(Fc)), 3.89–3.90 (m, 2CH(Fc)), 3.99 (s,

5CH(Fc)), 4.00–4.02 (m, 2CH(Fc)), 4.03–4.05 (m, 2CH(Fc)), 4.09–4.11 (m, 1CH(Fc)), 4.12–4.14 (m, 1CH(Fc)), 4.47 (s, CH), 4.51 (s, CH), 6.89 (d, $^{3}J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 6.97 (d, $^{3}J_{H,H}$ = 3.0 Hz, $CH_{arom.}$), 7.09 (dd, $^{4}J_{H,H}$ = 1.8 Hz, $^{3}J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 7.16 (dd, $^{4}J_{H,H}$ = 1.8 Hz, $^{3}J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 7.79 (d, $^{3}J_{H,H}$ = 5.4 Hz, $CH_{arom.}$), 7.84 (d, $^{3}J_{H,H}$ = 5.4 Hz, $CH_{arom.}$) ppm. ^{13}C NMR (two diastereoisomers, ca. 1:1): δ 53.3, 53.8 (2C, CH), 67.0, 67.1, 67.2, 67.4, 68.6, 69.2, 69.5, 69.6 (8C, CH(Fc)), 68.7 (s, 5C, CH(Fc)), 68.8 (s, 5C, CH(Fc)), 89.8, 91.3 (2C, C(Fc)), 127.8, 127.9, 128.6, 128.8, 128.9, 129.1 (6C, $CH_{arom.}$), 151.5, 152.7 (2C, $C_{arom.}$) ppm. IR: υ 3094 (m), 2892 (m), 2252 (w), 2107 (w), 2050 (w), 1768 (w), 1635 (w), 1597 (w), 1537 (w), 1461 (m), 1413 (m), 1277 (w), 1236 (m), 1106 (vs), 1027 (s), 999 (s), 921 (m), 815 (vs), 770 (m), 691 (vs), 485 (vs) cm^{-1}. Anal. calcd. for $C_{30}H_{26}Fe_2Se_2$ (656.14): C 54.92, H 3.99, found: C 55.12, H 4.22. HRMS (ESI): *m/z* calcd. for $C_{30}H_{26}Fe_2Se_2$ 657.90583; found 657.90715.

Ferrocenyl(2,2'-bithiophen-5-yl)methane (9)

Yield: 164 mg (45%). Yellow solid. M.p.: 94.0–96.0 °C. ^{1}H NMR: δ 3.87 (brs, CH_2), 4.12–4.14 (m, 2CH(Fc)), 4.16 (s, 5CH(Fc)), 4.17–4.19 (m, 2CH(Fc)), 6.69 (d, $J_{H,H}$ = 3.0 Hz, $CH_{arom.}$), 6.96–7.01 (m, 2 $CH_{arom.}$), 7.10 (dd, $^{4}J_{H,H}$ = 1.2 Hz, $^{3}J_{H,H}$ = 3.6 Hz, $CH_{arom.}$), 7.17 (dd, $^{4}J_{H,H}$ = 1.2 Hz, $^{3}J_{H,H}$ = 5.4 Hz, $CH_{arom.}$) ppm. ^{13}C NMR : 30.5 (1C, CH_2), 67.7, 68.4 (4C, CH(Fc)), 68.7 (s, 5C, CH(Fc)), 87.1 (1C, C(Fc)), 123.1, 123.3, 123.8, 125.2, 127.6 (5C, $CH_{arom.}$), 135.4, 137.8, 143.8 (3C, $C_{arom.}$) ppm. IR: υ 2930 (m), 2851 (m), 1514 (m), 1469 (m), 1425 (m), 1326 (m), 1280 (m), 1199 (m), 1105 (s), 1037 (m), 1023 (m), 999 (m), 837 (s), 788 (s), 756 (m), 695 (vs), 504 (s), 483 (m) cm^{-1}. Anal. calcd. for $C_{19}H_{16}FeS_2$ (364.31): C 62.64, H 4.43, S 17.60, found: C 62.75, H 4.61, S 17.39.

Acknowledgment

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